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Soil mobility of surface applied polyaromatic hydrocarbons in response to simulated rainfall

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Abstract

Polyaromatic hydrocarbons (PAHs) are emitted from a variety of sources and can accumulate on and within surface soil layers. To investigate the level of potential risk posed by surface contaminated soils, vertical soil column experiments were conducted to assess the mobility, when leached with simulated rainwater, of six selected PAHs (naphthalene, phenanthrene, fluoranthene, pyrene, benzo(e)pyrene and benzo(ghi)perylene) with contrasting hydrophobic characteristics and molecular weights/sizes. The only PAH found in the leachate within the experimental period of 26 days was naphthalene. The lack of migration of the other applied PAHs were consistent with their low mobilities within the soil columns which generally paralleled their log K_{oc} values. Thus only 2.3% of fluoranthene, 1.8% of pyrene, 0.2% of benzo(e)pyrene and 0.4% of benzo(ghi)perylene were translocated below the surface layer. The PAH distributions in the soil columns followed decreasing power relationships with 90% reductions in the starting levels being shown to occur within a maximum average depth of 0.94 cm compared to an average starting depth of 0.5 cm. A simple predictive model identifies the extensive time periods, in excess of 10 years, required to mobilise 50% of the benzo(e)pyrene and benzo(ghi)perylene from the surface soil layer. Although this reduces to between 2 and 7 years for fluoranthene and pyrene, it is concluded that the possibility of surface applied PAHs reaching and contaminating a groundwater aquifer is unlikely.

Keywords: Polyaromatic hydrocarbons, soil columns, simulated rainwater, leachate, mobility, hydrophobic characteristics, K_{oc} values.

1. Introduction

Polyaromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants, due to their release from both natural processes and anthropogenic activities, and because of their carcinogenic and mutagenic properties they have been classified as priority hazardous substances (EU WFD, 2000). A range of man-made diffuse sources exist with incomplete combustion processes leading to atmospheric emissions followed by subsequent deposition to available surfaces. Soils exhibit a particular affinity for PAHs which therefore tend to accumulate initially in the surface layers, potentially to environmentally critical concentrations (Mikkelsen et al., 1997) leading to a legacy of contaminated land (Wilson and Jones, 1993). The level of PAHs sorbed to soils is of concern due to the potential risk of eventual human exposure as a consequence of the subsequent leaching to groundwater (Wang et al., 2013) and/or uptake by growing crops allowing entry into the food chain (Watts et al., 2006).

Wilcke (2007) has investigated the patterns of PAH distributions in top soils throughout the world and found that the sum of the concentrations of 20 different PAHs ranged between 4.8 and 186,000 $\mu\text{g kg}^{-1}$ with naphthalene, phenanthrene and perylene predominating where contamination levels approached background concentrations. A number of studies have demonstrated the ready association of PAHs with urban soils (e.g. Mielke et al., 2001) while others have demonstrated their gradual decline in soils with increasing distances from man-made sources such as highways over longer distances (10 to 150 m) (Crepineau et al., 2003) and shorter distances (2 to 6 m) (Bryselbout et al., 2000). Vertical PAH distributions in soils have been less extensively studied and only usually at progressive depth increments of 10 or 15 cm despite Thuens et al. (2013) reporting considerable uncertainty when using a vertical sampling resolution of 5 cm to date PAH deposition in peat cores. Capuano et al. (2005) reported that the concentrations of total PAHs in soils impacted upon by a municipal solid waste incinerator decreased with depth from 318.9 $\mu\text{g kg}^{-1}$ (10 cm) to 88.9 $\mu\text{g kg}^{-1}$ (20 cm) to 74.1 $\mu\text{g kg}^{-1}$ (30 cm). Similarly, Banger et al. (2010) reported comparable decreases over three consecutive 15 cm depths of 2,364 $\mu\text{g kg}^{-1}$ to 839-1,104 $\mu\text{g kg}^{-1}$ to 251-456 $\mu\text{g kg}^{-1}$ in a commercial area soil. The majority of these studies, by reporting a snapshot reflecting the persistent input of PAHs at contaminated sites highlight the ability of

PAHs to contaminate soil at various depths but do not focus on temporal variation and only briefly consider the underlying factors governing vertical mobility.

A number of laboratory based approaches have been described for the investigation of the mobility of hydrophobic organic compounds, including PAHs, in soils and sediments. Stirred aqueous batch experiments have been frequently employed to study sorption and desorption processes (e.g. Chiou et al., 1998; Northcott and Jones, 2001) whereas column leaching methods accompanied by analysis of both the leachates and the soil column permit simulation of the downward soil movement of contaminants (Jackson et al., 1984). Similar experiments have identified the important role played by the quantity and quality of soil organic matter in controlling the leaching of PAHs from soils and sediments (Petruselli et al., 2002; Ran et al., 2007). Other controlling factors influencing the PAH leaching potential include the soil water ratio (Enell et al., 2004; Zand et al., 2010), residence time (Weigand et al., 2002), temperature (Enell et al., 2005), soil grain size (Zhang et al., 2008), soil aging (de Jonge, 2008), ionic strength of the leachate (Kim and Osako, 2003) and surfactant addition to the leachate (Frutos et al., 2011; Ganeshalingam et al., 1994).

In this paper, the leaching of freshly PAH contaminated soil surfaces (0-1 cm) within vertical soil columns are investigated using eluents with different ionic strengths. This approach is important as it contributes to the assessment of the potential of groundwater contamination by PAHs as well as having direct relevance to incidences of acute contamination such as that reported by Literathy et al. (2003) who studied the potential mobilisation of PAHs from the crude oil contamination of the upper soil layer in Kuwait following the Gulf War. In this study we concentrate on six selected PAHs (naphthalene, phenanthrene, fluoranthene, pyrene, benzo(e)pyrene and benzo(ghi)perylene) which are characterised by different molecular weights and ring structures as well as varying hydrophobic characteristics arising from their different organic carbon partitioning coefficients. The results provide a clear insight into the soil leaching behaviour of recently deposited surface PAHs enabling their mobility to be interpreted under conditions designed to simulate the relevant processes occurring in the natural unsterilized soil environment.

2. Experimental materials and methods

2.1. Soil sampling and characterisation

Surface soil samples (top 15 cm) were collected from two locations (A and B), representing different gravel terraces, at Sonning Farm (University of Reading), Berkshire, UK which is located on the alluvial plain of the River Thames. Soil A is a dark yellow-brown arable soil belonging to the Rowland Series whereas soil B is a dark brown acidic version of the Sonning Series which was collected from a wooded copse adjacent to the arable farmland. Soil samples were dried (48 h at 40 °C), sieved (< 2 mm) and analysed in triplicate for pH (as a soil water ratio of 1:2.5 (w/v)), maximum water holding capacity (MWHC), total organic carbon (Apollo 9000 TOC analyser) and particle size distribution. Particle size differentiation into three fractions (0.63 mm to 2 mm; 0.063 to 0.63 mm and < 0.063 mm) was achieved by sieving after mixing the soil samples (25 g) with sodium pyrophosphate. The finer fractions were further analysed using a laser particle size analyser (Fritsch Analysette Model 22) to enable identification of the relative proportions of sand, silt and clay fractions.

2.2. Leachate experiments

The leaching behaviours of the selected PAHs through the soil matrices were investigated using vertical columns conforming to OECD guidelines (OECD, 2004) for soil leaching column experiments. Glass columns (length 200 mm; internal diameter 50 mm) were carefully packed with 200 g of sieved soil (< 2 mm) using glass wool and glass beads (50 g, 3.5 mm diameter) to prevent soil loss from the bottom of each column. The soil was saturated from below and pre-equilibrated overnight with 0.01 M CaCl₂. The mixed PAHs (naphthalene, phenanthrene, fluoranthene, pyrene, benzo(e)pyrene, benzo(ghi)perylene) were introduced to the top of the column in the form of an artificially contaminated soil sample, prepared by fully mixing 5 g of soil with 5 ml of a PAH spiking solution in dichloromethane (1000 mg l⁻¹) (Fisher Scientific, UK), producing a slurry that upon dryness achieved a soil equivalent concentration of 1 mg g⁻¹ for each contaminant. The resulting dry contaminated soil was carefully introduced as a uniform 1 cm thick layer to the top of the soil column and a layer of glass wool and glass beads (25 g) positioned to protect the upper soil layers from disturbance by the incoming eluent. Each soil experiment was repeated in triplicate and identically prepared columns, without a contaminated surface soil layer, were established as controls. The elevated PAH concentration in the spiked top soil layer was selected to simulate the impact of leaching on heavily contaminated surface soils as well as ensuring confidence in the detection of leached PAHs. In addition, monuron, a herbicide which has been previously used as a reference compound in soil column leaching experiments (OECD, 2004) due to its known moderate soil leaching potential, was used throughout all experiments in parallel with the PAHs to validate the procedures and to serve as a positive control in comparison to the expected lower mobilities of the tested PAHs.

The leaching experiments were conducted over a period of 26 days by introducing 200 ml of 0.01M CaCl₂ (artificial rainwater) each day. This corresponds to an incremental liquid-to-solid ratio of 0.975 l kg⁻¹ for each day of leaching with a maximum value of 25.35 l kg⁻¹ being reached after 26 days. An average percolation rate of 8.3 ml h⁻¹ was maintained and after 15 days the leaching solution for one of the columns for each soil plus the control columns was changed to 0.1M NaCl solution to assess the impact of increasing the ionic strength of the leachate. Column eluents were collected daily and combined for consecutive two day periods prior to determination of pollutant levels and dissolved organic carbon (DOC) (triplicate analysis using a Shimadzu TOC-V CPN instrument). On completion of the leaching process, each soil column was carefully removed and divided into vertical segments corresponding to soil depths of 0-1 cm, 1-2 cm, 2-3 cm, 3-5 cm, 5-7 cm and greater than 7 cm. The soil samples were air dried for two days and subsequently stored at -10 °C prior to extraction.

2.3. PAH and monuron extraction and analysis

PAH and monuron extractions from the spiked soils (1 g) and column segments (5 g) were achieved ultrasonically (3 x 1h sonication) using dichloromethane (25 ml). Following filtration of the resulting extract, residues were reconstituted with a known volume of dichloromethane depending on their derivation as shown below:

- 1 ml for extracts from the column below the 0-1 cm layer
- 10 ml for extracts from the top contaminated 0-1 cm layer
- 100 ml for extracts from the spiked soil

Concentrated extracts were analysed in duplicate using gas chromatography-mass spectrometry (GC-MS). The collected column leachates were passed through solid phase extraction (SPE) cartridges (StrataX, 200 mg/3 ml, 8B-S100-FBJ, Phenomenex, UK) which had been previously activated with methanol followed by a deionised water wash. Dichloromethane (6 ml introduced as 3 x 2 ml aliquots) was used to elute the retained compounds and after controlled evaporation to dryness the residue was re-dissolved in dichloromethane (1 ml) and the reconstituted sample analysed by GC-MS.

A Shimadzu GC-2010 gas chromatograph coupled with a GC-MS-QP2010 detector utilising electron impact ionisation was used for all PAH analyses after separation on a DB-5MS capillary column (30m x 0.25mm i.d. x 0.25 µm film thickness). 2 µl samples were injected in split mode, using helium as the carrier gas with an on-column flow rate of 2.12 ml min⁻¹. The injection port was held at 250 °C, the ion source temperature at 200 °C and the outlet to the mass spectrometer at 310 °C. The oven temperature was initially programmed at 100 °C for 2 minutes, then ramped at a rate of 10 °C min⁻¹ to 180 °C, held for another 2 minutes before ramping again at a rate of 4 °C min⁻¹ to 300 °C giving a total run time of 42 minutes. Selected ion monitoring (SIM) was used to facilitate quantitative analysis with calibration (US EPA, 1984) based on an external standard containing the 16 US EPA regulated PAHs (Sigma-Aldrich, UK). The following m/z values were used as quantifier ions and qualifier ions (in brackets): naphthalene, 128 (64); phenanthrene, 178 (76, 152); fluoranthene, 202 (200,101); pyrene, 202 (100, 101); benzo(e)pyrene, 252 (126, 125); benzo(ghi)perylene, 276 (138, 137). For monuron analysis the GC-MS parameters were modified slightly with the oven temperature reduced to 110 °C for 5 minutes to achieve a retention time of 3.48 minutes. The thermal degradation product of monuron, 4-chlorophenyl isocyanate was detected using SIM mode (m/z values: 90, 125, 150). All sample analyses were replicated and consistently validated against appropriate standards and blank solutions.

3. Results and Discussion

3.1. Soil characteristics

The determined characteristics of the two soils are presented in Table 1 and demonstrate the more acidic nature of soil B compared to soil A which is effectively neutral. Soil A possesses a lower organic content than soil B, which can be explained by the more intense cultivation to which it has been exposed. It also exhibits a higher MWHC which is consistent with its arable use. Particle size analysis indicates that both soils contain over 70% in the sand fraction but that soil A possesses a higher contribution of the finer grain sizes associated with clays and particularly silts.

Monuron and naphthalene were not observed in either of the collected soils (detection limit 6 µg kg⁻¹). The background concentrations of the remaining individual PAHs in soils A and B are shown in Table 1 and are consistent with other published results on the levels of PAHs in temperate top soils but at the lower end of the concentration ranges reported by Nam et al. (2008) for background PAH levels in soils from grassland sites within the UK. This is indicative of low atmospheric inputs at the collection site. The background PAH levels were subtracted from all determined values in the soil column experiments.

Table 1. Physico-chemical characteristics and background PAH concentrations of soils A and B.

	Soil A (mean \pm SD)	Soil B (mean \pm SD)
pH		
In deionised water	7.22 \pm 0.05	4.22 \pm 0.01
In 0.01M CaCl ₂	6.44 \pm 0.04	3.52 \pm 0.01
Maximum Water Holding Capacity (%)	44.3 \pm 3.8	12.0 \pm 1.0
Total Organic Carbon (mg kg ⁻¹)	8285 \pm 331	36494 \pm 2686
*Particle size distribution (%)		
Sand (0.02-2 mm)	73	82
Silt (0.002-0.02 mm)	23	16
Clay	4	2
Background PAH concentrations (μ g kg ⁻¹)		
Naphthalene	< 6	< 6
Phenanthrene	10 \pm 2	110 \pm 15
Fluoranthene	30 \pm 12	250 \pm 37
Pyrene	30 \pm 11	200 \pm 27
Benzo(e)pyrene	10 \pm 2	60 \pm 3
Benzo(ghi)perylene	10 \pm 2	60 \pm 5

*Soil size fractions are according to the International Soil Science Society

SD = standard deviation

3.2. Extraction technique validation

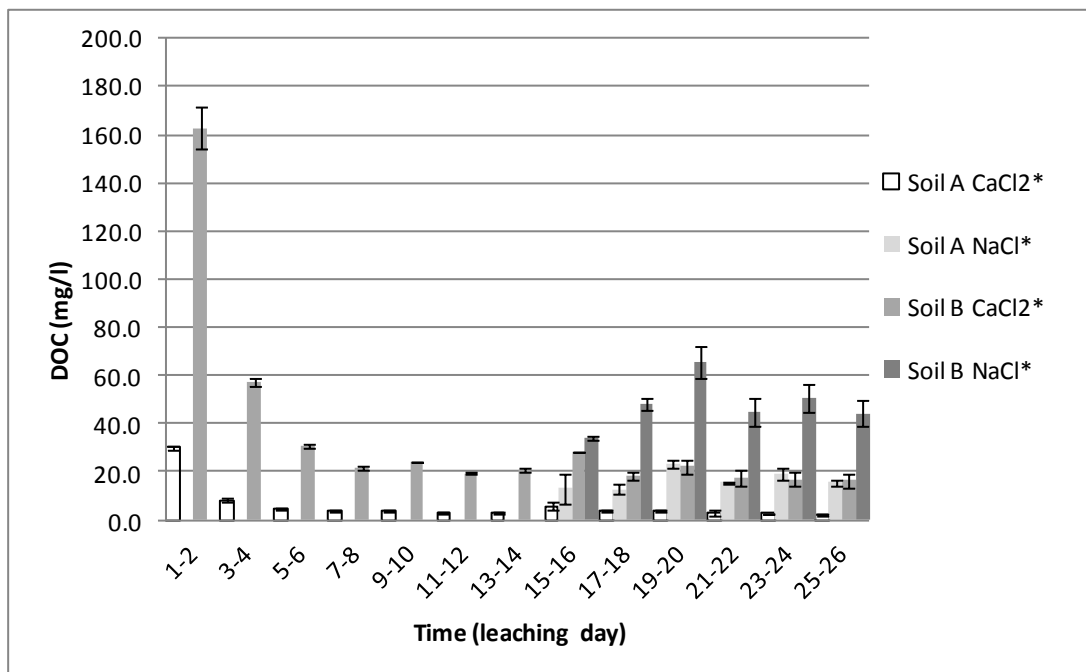
The efficiencies of the employed extraction techniques for PAHs and monuron were tested using both a prepared spiking solution and the artificially contaminated soils. The mean results together with the determined percentage recoveries are tabulated in Online Resource 1. The variabilities in the results obtained for the spiking solution can be partly explained by the use of an external standard in which the analytes were dissolved in pure dichloromethane and were not influenced by matrix effect factors (Zhang, 2011). The percentage recoveries achieved by the ultrasonic extraction of the contaminated soils also show variations with values in excess of 100% for phenanthrene, fluoranthene and pyrene for both soils. These enhanced positive results are consistent with matrix effects increasing the response of the analytical instrument as has been described by Hajslova and Zrostlikova (2003) for the trace analysis of pesticides from various matrices. The less efficient recoveries recorded for benzo(e)pyrene (60%) and benzo(ghi)perylene (39%) are consistent with the stronger attachment of these higher molecular weight PAHs to soil particles. Northcott and Jones (2001) have reported a decrease in the extractability of PAHs with increasing molecular weight as well as with increasing octanol-water partitioning coefficient (K_{ow}) and organic carbon normalised soil-water partitioning coefficient (K_{oc}) values. The poor recoveries of naphthalene are believed to be related to evaporative losses as evidenced by a Henry's Law constant of 4.4×10^{-4} atm m³ mole⁻¹ which progressively increases with the molecular weight of the studied PAHs reaching a value of 2.66×10^{-7} atm m³ mole⁻¹ for benzo(ghi)perylene. Monuron was recovered at extraction efficiencies of 65% and over. The recovery efficiencies obtained for the spiked solutions and soils were used to correct the PAH extraction amounts monitored during the leaching experiments.

3.3. Column leaching experiments

3.3.1. Dissolved organic carbon content

DOC has been monitored for the column leachates as its presence is known to be able to increase the mobility of hydrophobic organic compounds, such as PAHs, through binding mechanism to macromolecules, such as humic and fulvic acids. Naes et al. (1998) demonstrated that up to 90% of the total concentration of individual PAHs in the receiving waters of an aluminium plant was accounted for by the DOC-associated phase and Magee et al. (1991) showed that the formation of a phenanthrene – DOM 'complex' almost doubled its mobility through a sand column. The average DOC concentrations in the 2 day combined leachate samples are shown in Figure 1 and clearly demonstrate the differences in the soil organic contents and mobilities of the two soil types with the concentrations (mean \pm s.d.) leaching from soil A progressively decreasing from 29.9 ± 1.0 mg l⁻¹ to 2.4 ± 0.4 mg l⁻¹ during the final days of the experiment when the eluent was maintained as 0.01M CaCl₂. The total amount of DOC released was 78.9 mg which represents 1.9% of the organic carbon initially available in the soil column. The leachate DOC values for the more highly organic soil B

ranged from $162.9 \pm 8.6 \text{ mg l}^{-1}$ to $16.3 \pm 3.2 \text{ mg l}^{-1}$ over the course of the experiment with 456.3 mg (2.4%) being released from the soil column. The introduction of 0.1M NaCl solution as the eluent on leaching day 15 increased the DOC concentration with this effect being most pronounced after 20 days. The percentage of the available organic carbon effectively doubled to 3.7% for soil A with a lower enhancement to 3.3% for soil B. There is considerable debate concerning the effect of ionic strength on the mobilisation of DOC from soils (Kalbitz et al., 2000) but evidence exists that chemical interactions with Na ions facilitate the release of DOC (Skylberg and Magnussen, 1995) compared to Ca ions which enhance its precipitation (Romkens and Dolfing, 1998). These phenomena are supported by the results reported here.



*CaCl₂ indicates that only 0.01M CaCl₂ was used for leaching

*NaCl indicates that after 15 days the leaching solution was changed to 0.1M NaCl

Error bars represent standard deviations relative to the mean value of triplicate column experiments

Figure 1. Temporal variations in DOC concentrations in the soil column leachates.

3.3.2. Mass balances for PAHs

PAH mass balances have been derived by comparing the combined amounts in the collected leachate samples and remaining in the soil columns at the end of the 26 day leaching experiments with the measured amounts initially applied in the artificially contaminated soil layer. No PAH was found in the leachate, except for naphthalene for which the amounts were $2.7 \pm 0.4 \mu\text{g}$ for soil A and $3.0 \pm 0.3 \mu\text{g}$ for soil B, which represented only a minute proportion (<0.1%) of that originally introduced. Therefore, although more mobile than the other monitored PAHs, the full leaching potential for naphthalene was very limited for both studied soils.

Overall recoveries of PAHs at the end of the 26 day leaching period varied considerably (Table 2) and can be attributed to a number of explanatory variables including the volatility of PAHs containing less than 3 rings (Park, 1990), the elevated biodegradability of 2- and 3-ring PAHs (Reid et al., 2001; Tabak et al., 1981; Herbes and Schwall, 1978) as well as strong sorption to soil organic matter of larger PAHs (Alexander, 1995; Weissenfels et al., 1992). The absence of PAHs (other than naphthalene) in leachate is consistent with the work of Reemtsma and Mehrtens (1997) who demonstrated that the released fractions of PAHs in column leaching experiments decreased with increasing molecular size and hydrophobicity of the compound with 5 ring PAHs not being leachable even under highly favourable column conditions (Zand et al., 2010).

Table 2. Overall recoveries of PAHs and monuron at the end of the experimental leaching period.

	Soil column A			Soil column B		
	Mean percentage recovery	Mean recovered amount (mg)	RSD%	Mean percentage recovery	Mean recovered amount (mg)	RSD%
Naphthalene	0.59	0.01	10.9	0.77	0.03	16.0
Phenanthrene	30.4	1.89	18.8	14.4	0.83	27.3
Fluoranthene	63.6	3.71	23.3	86.4	4.64	5.4
Pyrene	86.4	5.23	6.0	92.9	5.10	5.2
Benzo(e)pyrene	105.4	2.92	2.8	123.0	3.33	13.5
Benzo(ghi)perylene	125.5	2.70	15.4	155.6	3.34	5.4
Monuron	63.0	2.15	1.6	58.3	2.23	12.2

RSD%: relative standard deviation of results from triplicate columns

Monuron was utilised to ensure the packed columns were operating efficiently. The observed temporal leaching patterns indicated that the majority of the leached compound passed through soil A columns during the early stages of the experiment (75% in the first 2 days) whereas for soil B a more prolonged retention was observed (34% released in the first 4 days) with small amounts of monuron still appearing after 26 days. This was paralleled, although on a much reduced scale, by the leaching behaviour of naphthalene which may suggest the presence of some initial channelling in soil A providing preferential pathways (Jackson et al., 1984). Despite the different temporal characteristics demonstrated by monuron, very similar total amounts were released in the leachates from soil A ($2144 \pm 34 \mu\text{g}$) and soil B columns ($2175 \pm 265 \mu\text{g}$).

3.3.3. PAH distribution in the soil columns

Naphthalene demonstrated low levels remaining within the soil columns ($11 \pm 1.1 \mu\text{g}$ in soil A; $23 \pm 3.7 \mu\text{g}$ in soil B) and with the majority retained within the surface layer. The losses of naphthalene from the soil columns are mainly attributed to volatilisation due to its elevated Henry's Law constant compared to the other tested PAHs. Park et al. (1990) observed that volatilisation accounted for losses of 30% from two different soils under unsaturated conditions and Lors et al. (2012) monitored the complete elimination of 2-ring PAHs in laboratory experiments conducted on PAH contaminated soils. There is also the possibility of microbial degradation as the soils were not sterilised and half-lives of the order of 2 days have been determined for naphthalene in soils (Park et al., 1990). The potential for phenanthrene to undergo biodegradation is indicated by half-lives between 7 and 34 days with almost complete degradation (94%) in the soil environment after 3 months (Lors et al., 2012). The impact of biodegradation losses for phenanthrene in the soil column experiments is exemplified by the the total amounts retained at the end of the leaching experiment representing only 30.4 % (soil A) and 14.4 % (soil B) of that applied. Additionally, there was evidence of some phenanthrene reaching the lower levels of the soil columns (Online Resource 2) although the majority was retained in the spiked 0-1 cm layer. Because of the low overall recoveries obtained for naphthalene and phenanthrene, they are not considered further in the interpretation of PAH behaviours in soil columns.

The limited movements of fluoranthene, pyrene, benzo(e)pyrene and benzo(ghi)perylene in the soil columns after 26 days of leaching are demonstrated by the low percentages which have penetrated below the top 1 cm of soil compared to the total amounts retained on the columns (Table 3). Less than 3% was translocated from the surface layer within both soils in agreement with the observed low mobility of PAH fractions in column experiments (Enell et al., 2004; Bauw et al., 1991). In batch experiments, Kim and Osako (2003) observed leaching amounts of 1.7% for phenanthrene and 3.9% for pyrene from sandy soils.

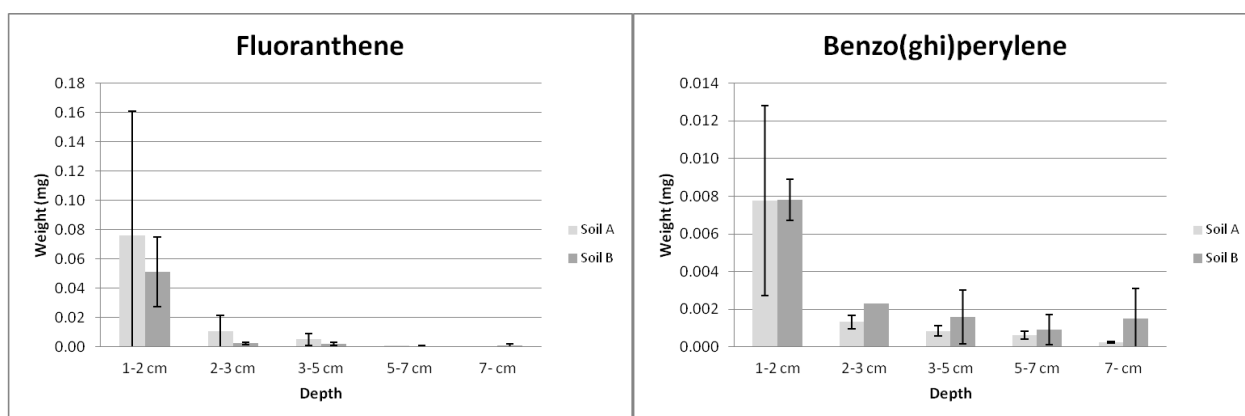
Table 3. Tabulated summary of PAH distributions in soils and model predictions following 26 day leaching experiments with CaCl₂.

	Soil A				Soil B			
	Measured over 26 days		Predicted values		Measured over 26 days		Predicted values	
	% mobilised below spiked layer (0-1 cm) (mean \pm SD)	Average soil depth to reduce starting PAH level by 90%	Average soil depth to reduce starting PAH level by 90% over 1 year	Predicted time (years) to deplete PAH level in the 0-1 cm layer by 50%	% mobilised below spiked layer (0-1 cm) (mean \pm SD)	Average soil depth to reduce starting PAH level by 90%	Average soil depth to reduce starting PAH level by 90% over 1 year	Predicted time (years) to deplete PAH level in the 0-1 cm layer by 50%
Phenanthrene	3.49 \pm 1.41	N/A	N/A	N/A	2.98 \pm 2.18	N/A	N/A	N/A
Fluoranthene	2.26 \pm 1.99	0.94 cm	1.30 cm	2.2	1.16 \pm 0.40	0.87 cm	1.11 cm	4.4
Pyrene	1.83 \pm 0.90	0.90 cm	1.23 cm	2.6	0.63 \pm 0.21	0.73 cm	0.99 cm	6.6
Benzo(e)pyrene	0.24 \pm 0.13	0.68 cm	0.94 cm	19.8	0.23 \pm 0.05	0.64 cm	0.92 cm	27.7
Benzo(ghi)perylene	0.40 \pm 0.16	0.70 cm	1.01 cm	13.4	0.43 \pm 0.14	0.66 cm	1.00 cm	16.0

Mean and standard deviation (SD) values are for triplicate soil column experiments; N/A=not applicable for phenanthrene.

The small amounts of PAHs passing into the deeper soil sections are consistent with their K_{oc} values and similarities exist between fluoranthene and pyrene and between benzo(e)pyrene and benzo(ghi)perylene in the two different soils in terms of their abilities to penetrate below a depth of 1 cm. These behaviours are illustrated for fluoranthene and benzo(ghi)perylene in Figure 2. Soil A demonstrates a slightly lower retention capability for both fluoranthene and pyrene compared to the more organic soil B with fluoranthene demonstrating a slightly enhanced leaching potential (consistent with its lower K_{oc} value). Benzo(e)pyrene and benzo(ghi)perylene showed comparable affinities for both soils below the surface layer but surprisingly benzo(ghi)perylene leached slightly more efficiently, which is not consistent with the trend in K_{oc} values. It is also noticeable that the minimal levels of the heavier PAHs reaching the lowest soil depth are comparable to those of fluoranthene and pyrene. This is believed to be due to the existence of a small amount of channelization which influenced the results for the heavier PAHs in one of the columns. However, the overall influencing factor on the soil penetration of different PAHs is the K_{oc} value with a clear linear relationship demonstrating decreasing mobility with increasing K_{oc} (Figure 3). Zhang et al. (2008) and Enell et al. (2004) have shown an equivalent dependence of leaching ability on K_{ow} values. The correlation is considerably stronger for soil A ($r^2 = 0.90$) possibly due to the lower organic content whereas for soil B ($r^2 = 0.58$), the higher organic content appears to exert a more pronounced impact on the lighter PAHs, increasing their retention relative to that which occurs in soil A. The soil organic matter contains both aromatic and aliphatic groups with the former being responsible for the preferred solid partitioning of PAHs (Chiou et al., 1998).

In some of the columns, the leaching solution was changed from 0.01M CaCl₂ to 0.1M NaCl after 15 days of percolation to assess the possible impact of the increased mobility of DOC on the movement of the PAHs due to their affinity for organic matter, particularly dissolved humic material which has been shown to produce an increased apparent aqueous solubility of PAHs (Lassen et al., 1997). This effect is considerably less pronounced for PAHs with the lowest aqueous solubilities since leaching solution change had no impact on the heavier PAHs (benzo(e)pyrene and benzo(ghi)perylene) in either soil. However, for the lighter and more soluble PAHs (fluoranthene and pyrene) there was a greater increase in mobilisation in soil A as demonstrated by a 5-fold increase to 171 μ g in the amount of fluoranthene reaching the 1-2 cm soil layer compared to a 100% increase to 9 μ g in the 3-5 cm layer in soil A. The increases were less dramatic in soil B with a doubling of the mobilised amounts of fluoranthene (to 68 μ g) and pyrene (to 40 μ g) although this was confined to the 1-2 cm soil layer. A similar increased leaching potential as a consequence of enhanced DOC levels has previously been demonstrated for phenanthrene and pyrene (de Jonge et al., 2008; Kim and Osako, 2003).



Error bars represent standard deviations relative to the mean value of triplicate column experiments

Figure 2. Distributions of fluoranthene and benzo(ghi)perylene at depths greater than 1 cm in soil columns A and B after leaching with CaCl_2 for 26 days.

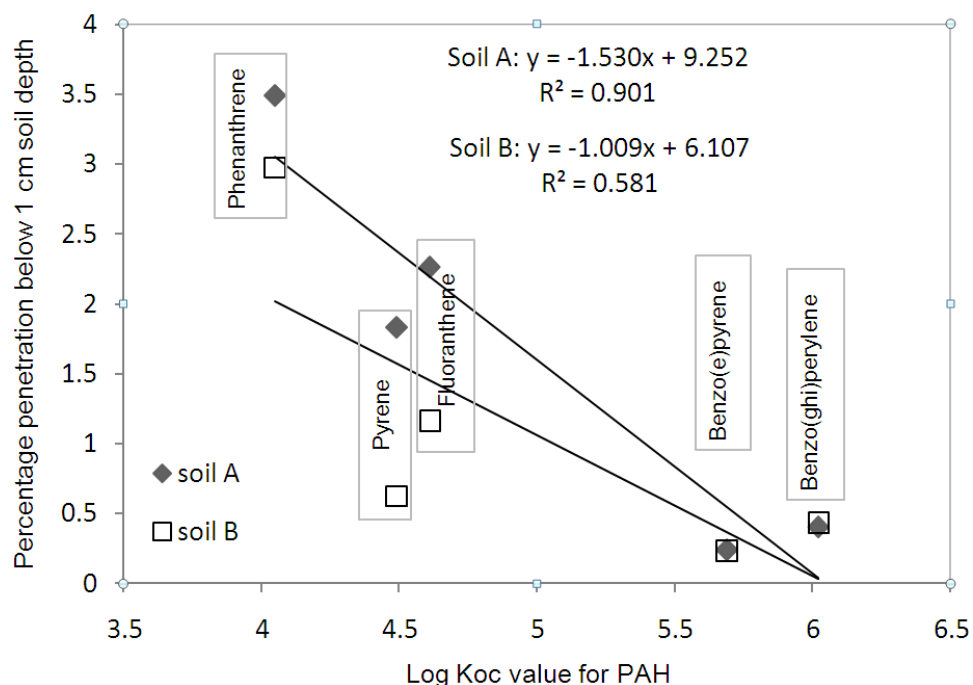


Figure 3. Relationship between K_{oc} values and average PAH percentages penetrating below 1 cm depth in soil columns.

3.4. Modelling predictions based on experimental results.

3.4.1. Soil depth penetration

The soil column leaching experiments have provided evidence for the limited mobilisation of the analysed PAHs within the soil matrices to a depth of 7 cm over a duration of 26 days as well as the rapid decreases in PAH levels below the 0-1 cm surface layer in both soils linked with increasing PAH molecular weight and associated water solubilities of the individual compounds. Jones et al. (1989) found that PAH leaching rates were strongly influenced by the existence of

DOC mediated or particle associated transport and Petruzelli et al. (2002) have identified the different roles played by humic and fulvic acids in controlling the vertical leaching of PAHs with the former enhancing retention whereas fulvic acids favoured an increase in PAH mobility. For the PAHs recovered at levels greater than 50% (i.e. fluoranthene, pyrene, benzo(e)pyrene and benzo(ghi)perylene), this study confirms the conflicting roles of released DOC and the organic content of the soil.

Fluoranthene and pyrene are able to penetrate to greater depths below the surface layer than benzo(e)pyrene and benzo(ghi)perylene due to their lower K_{oc} values. The PAH leaching patterns throughout the soil columns demonstrate rapid decreases in PAH levels below the 0-1 cm surface layer in both soils which can be represented mathematically by power relationships. These can be used to predict the soil depths which would be required to reduce by 90% the amount of each PAH originally existing in the surface layer (Table 3). Figure 4a demonstrates this pattern throughout the entire soil column for pyrene in soils A and B together with the power equations which describe the decreases. To identify the discrimination which exists between the two soils, Figure 4b shows the decreasing trend but only below the surface layer. The average soil depths provided in Table 3 for fluoranthene, pyrene, benzo(e)pyrene and benzo(ghi)perylene represent the mid-points of the respective surface layers e.g. 0.5 cm represents the 0-1 cm contaminated surface layer and 1.5 cm would represent the underlying 1-2 cm layer etc.

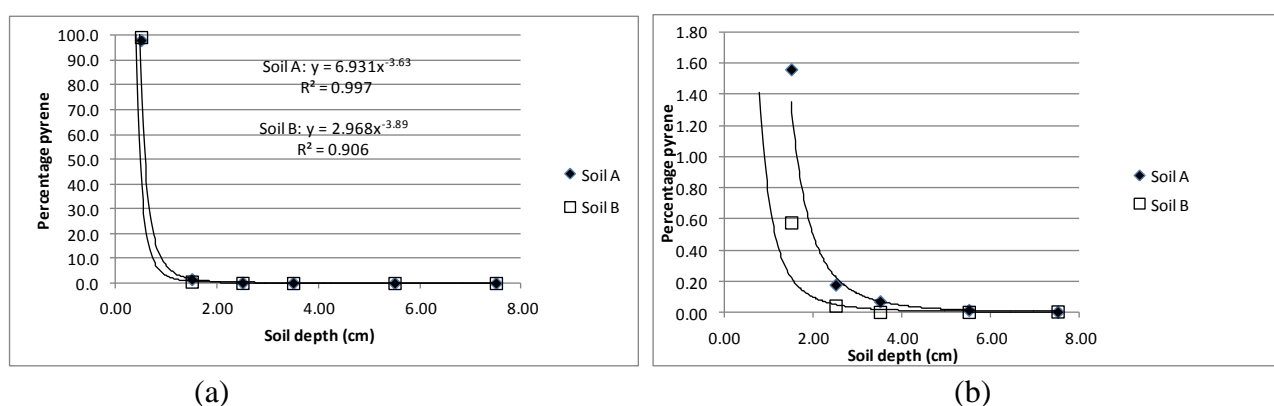


Figure 4. Representations of the decreases with depth over 26 days of (a) pyrene throughout the entire soil column and (b) pyrene below the surface layer (0-1 cm) in soils A and B.

Table 3 demonstrates the limited depths (0.64–0.94 cm) to which the PAHs were able to penetrate before being reduced to 90% of the starting level in the surface layer (0-1 cm). There are clear similarities between the behaviours of fluoranthene and pyrene, which in agreement with their K_{oc} values, were able to penetrate further into the soil (0.90-0.94 cm in soil A) compared to benzo(e)pyrene and benzo(ghi)perylene (0.68-0.70 cm in soil A). Comparisons of the same PAHs in soils A and B indicate that a more rapid reduction consistently occurs in soil B due to the influence of the higher organic carbon content in this soil. The differences in the soil behaviours are greatest for the lower molecular weight PAHs with pyrene demonstrating the greatest discrimination in terms of its behaviour in soils A and B despite the similarities in the log K_{oc} values for fluoranthene (4.48) and pyrene (4.23). In addition to sorption onto outer humic surfaces, it has been postulated that PAH diffusion is also controlled by the narrow meso- and micro-pores of geomaterials where these are of a comparable molecular size (Abu and Smith, 2006; Nam and Alexander, 1998). It would appear that this factor becomes important in the case of the heavier PAHs (benzo(e)pyrene and benzo(ghi)perylene) enabling them to penetrate further into soil B due to its higher coarse sand fraction (Table 1) and resulting in similar removal depths for both soils despite the higher organic content of soil B.

3.4.2. Temporal soil depth predictions

Knowledge of the long term movement of PAHs within the deeper segments of a contaminated surface soil is necessary to determine their final destination in relation to underlying aquifers and hence any potential to cause contamination. Based on the 26 day experimental PAH leaching rate results, it is possible to estimate the temporal variation in the deeper subsurface soil segments using the PAH mobilisation patterns observed in the column experiments (Table 3; Figure 4b). A proposed simple predictive approach assumes that the PAH transfer from each contaminated upper soil layer remains constant for each compound and the derived overall rate of mobilisation is repeatedly applied for each 26 day period (the time of the leaching experiment). Although this scenario is unlikely to be strictly true in practice as the PAH movement between different soil layers may be restricted as sub-soil contamination increases, the low

amounts of PAHs detected in the majority of the different lower soil layers will minimise the impact of this process. By taking into account the impact of PAH depletion in the top soil layer, the PAH transfer between the two upper soil layers can be derived for different time periods. For example, the leaching percentage of pyrene from the top 0-1 cm layer of soil A to the 1-2 cm layer after 26 days was 1.56% (Figure 4b) with the predicted amounts for the subsequent three 26 day periods being 3.10%, 4.61% and 6.10%. Continuation of this mathematical approach leads to a time dependent power relationship for the transfer of pyrene between the two upper layers:

$$y = 1.589x^{0.963} \quad (R^2 = 0.999)$$

where y = % pyrene transferring between the 0-1 cm and the 1-2 cm soil layers

x = number of 26 day periods which have elapsed

Similar power equations can be developed for the transfer of pyrene between deeper soil layers and used to predict the future distributions of pyrene and, using the same approach, the other PAHs in the sub-surface soil layers. The changing distribution patterns between those experimentally determined after 26 days and the predicted results after 14 consecutive 26 day periods (364 days; approximately 1 year) for both soils are shown in Figure 5 for fluoranthene and benzo(ghi)perylene. Although the role of PAH biodegradation has not been accounted for, this is expected to be limited due to a decreasing PAH availability in aged-contaminated soils (Cebon et al., 2013).

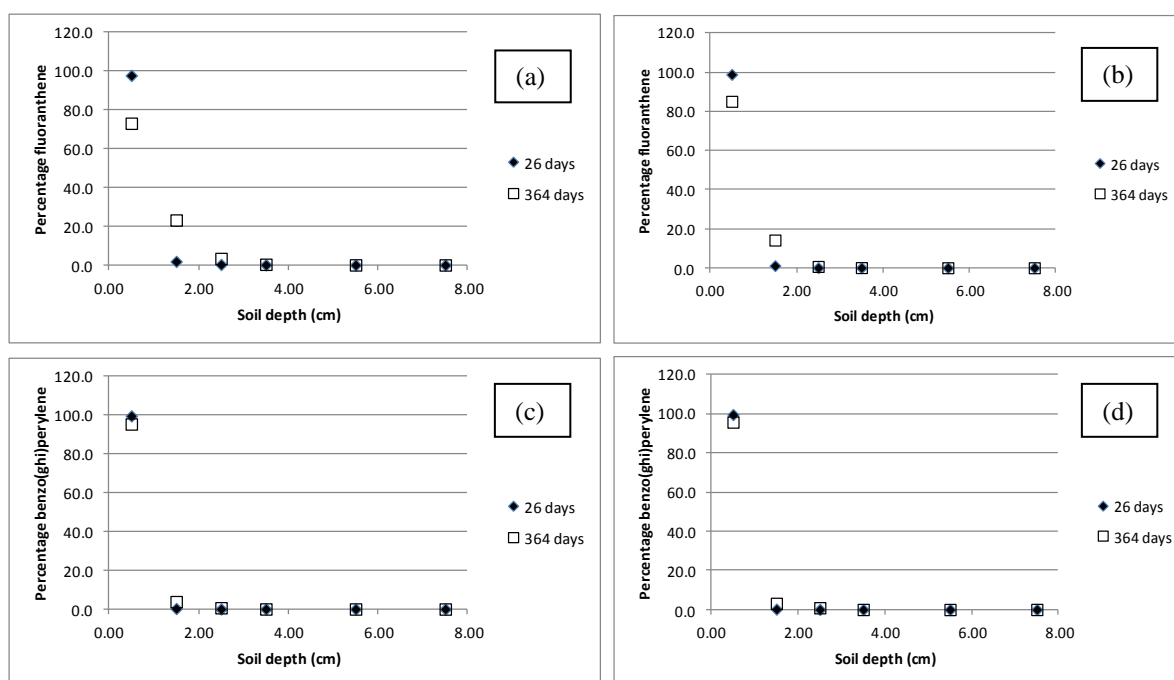


Figure 5. Measured soil depth penetration after 26 days and predicted soil depth penetration after 364 days for (a) fluoranthene in soil A, (b) fluoranthene in soil B, (c) benzo(ghi)perylene in soil A and (d) benzo(ghi)perylene in soil B.

The potential soil movement of fluoranthene is clearly more enhanced than that of the heavier benzo(ghi) perylene molecule in both soils although this is effectively limited to reaching only the 1-2 cm layer. The amounts of applied fluoranthene predicted to reach the 1-2 cm soil depth after 1 year in soils A and B are 23% and 14%, respectively and for benzo(ghi)perylene this reduces to 4% and 3%, respectively. The soil penetration capability to the 2-3 cm layer reduces to 3% for fluoranthene in soil A and to only 1% in the more organic soil B. The behaviours of the different PAHs after 1 year can also be interpreted from the average depths to which they are predicted to penetrate before a 90% reduction of the initial amount has occurred as shown in Table 3. The discrimination in penetrating ability is similar to that observed over the 26 day experimental period but with a stronger relative tendency for the movement of benzo(ghi)perylene compared to benzo(e)pyrene. This would appear to infer that over longer leaching periods the influence of particulate organic carbon adsorption is more fully balanced by other controlling factors such as the ability of a PAH to infiltrate through the soil pore structure.

For all the studied PAHs, penetration below the 2-3 cm layers of both soils is negligible indicating that a 3 cm depth represents a barrier below which PAHs are unlikely to leach over a 1 year period even under the most favourable infiltrating conditions. The different behaviours of the PAHs in the upper soil layers, as well as their collective low mobilities, can be expressed by using the predictive approach to obtain the expected time taken for 50% of the contaminant to be transferred from the 0-1 cm contaminated soil layer (Table 3). The higher retentive capabilities of soil B are demonstrated by at least a doubling of the time taken for 50% of fluoranthene and pyrene to be released from the upper layer. The time comparisons between the two soils are less marked for the less mobile PAHs with higher log K_{oc} values (benzo(e)pyrene and benzo(ghi)perylene). The estimated timescales, ranging from a minimum of 2.2 years for fluoranthene in soil A to a maximum of 27.7 years for benzo(e)pyrene in soil B, illustrate the improbability that the PAHs could eventually reach soil depths where they would have the potential to contaminate groundwater aquifers. The envisaged risks would be even lower if the perceived losses due to evaporation and/or microbial biodegradation were included in the adopted predictive framework over the extended time periods.

4. Conclusions

Column leaching experiments have been used to determine the downward mobilities within two different soils of four surface applied PAHs (fluoranthene, pyrene, benzo(e)pyrene and benzo(ghi)perylene). Although soil pore size influences the behaviours of the two heavier PAHs, it is the organic carbon interactions which play the major part in controlling the PAH movement. It has been shown that higher dissolved organic carbon levels in the leachate increase the mobilisation of the lighter PAHs but the major controlling factor is the particulate organic carbon which reduces, to negligible amounts, the abilities of fluoranthene and pyrene to penetrate below soil depths of 2 cm. The diminishing PAH levels within the soil column follow a decreasing power relationship over a monitored 26 day leaching period with 90% reductions consistently occurring at average soil depths not exceeding 1 cm. By employing a simple modelling approach, the PAH penetration over a 1 year period of continuous infiltrating conditions is shown to be negligible below the 2-3 cm soil layer. The long term downward depth attenuation will also be further limited by potential biodegradation processes which were not part of this investigation. The immobility of the studied PAHs is also demonstrated by the predicted times required for a 50% depletion of the contaminated surface layer which exceed 10 years for benzo(e)pyrene and benzo(ghi)perylene and range between 2 and 7 years for fluoranthene and pyrene. The limited soil mobilities of PAHs containing more than 3 aromatic rings suggest that there is very little possibility of them reaching and contaminating a groundwater aquifer. Where these PAHs have been found in sub-soils at depths of 5 cm and below it is highly probable that a historical pattern involving repeated long term deposition is responsible rather than surface leaching processes.

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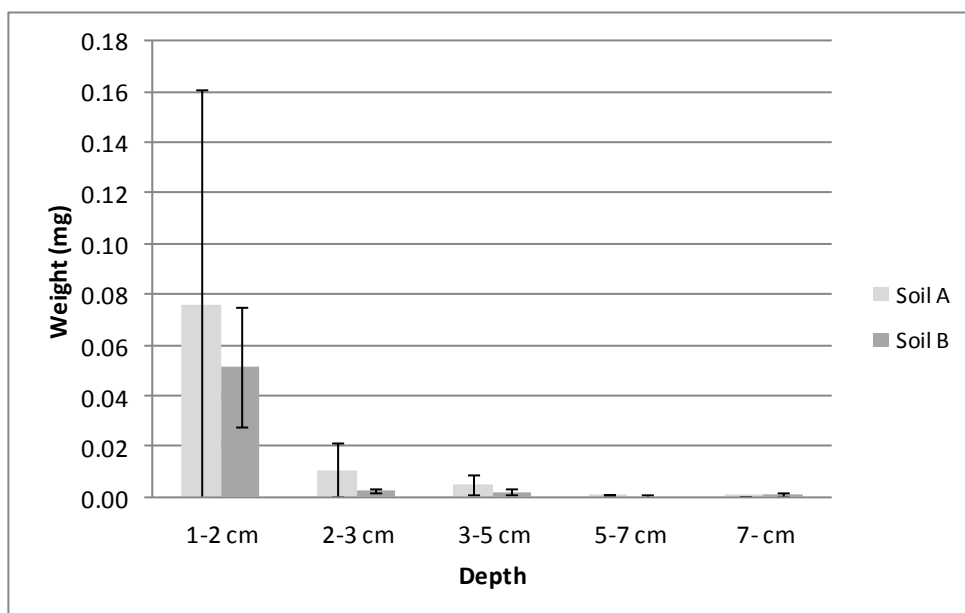
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ONLINE RESOURCES

Online Resource 1. Analysed levels of PAHs and monuron in the prepared spiking solution (1000 mg l^{-1}) and extraction recovery efficiencies from the artificially contaminated soil sub-samples (nominally 5 mg g^{-1})

	Spiking solution			Soil A		Soil B	
	Mean concentration (mg l^{-1})	RSD%	Mean weight in 5 ml (mg)	Weight of compound (mg) (mean \pm SD)	Mean percentage recovery	Weight of compound (mg) (mean \pm SD)	Mean percentage recovery
Naphthalene	1049.4	6.1	5.25	2.24 (± 0.03)	42.6	3.42 (± 0.09)	65.1
Phenanthrene	989.2	1.7	4.95	6.21 (± 0.07)	125.5	5.72 (± 0.16)	115.6
Fluoranthene	944.6	6.1	4.72	5.83 (± 0.11)	123.5	5.37 (± 0.07)	113.6
Pyrene	976.5	5.8	4.88	6.05 (± 0.03)	124.0	5.49 (± 0.13)	112.4
Benzo(e)pyrene	905.7	0.3	4.53	2.77 (± 0.27)	61.3	2.71 (± 0.05)	59.9
Benzo(ghi)perylene	1100.4	2.5	5.50	2.15 (± 0.18)	39.0	2.15 (± 0.05)	39.0
Monuron	1050.1	3.9	5.25	3.41 (± 0.32)	65.0	3.82 (± 0.05)	72.7

RSD%: relative standard deviation of duplicate analyses



Error bars represent standard deviations relative to the mean value of triplicate column experiments

Online Resource 2. Distributions of phenanthrene at depths greater than 1 cm in soil columns A and B after leaching with 0.01M CaCl_2 for 26 days.